

## **P-V-T and Phase Equilibrium Data of a R32-R125 Refrigerant Mixture<sup>1</sup>**

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**ABSTRACT**

The volumetric behavior of the refrigerant binary mixture of R32 and R125 (difluoromethane and pentafluoroethane) containing 0.1902 mass fraction of R32 was studied by the method of constant volume piezometer in a wide range of temperatures. The standard error of the density measurements was not more than 0.1% with the confidence probability of 0.95. The results obtained during the present investigation were generalized in the entire temperature range by means of the uniform equation of state written in a form of the Benedict-Webb-Rubén correlation.

KEY WORDS: density; equation of state; experimental method; gas phase; liquid phase; phase equilibrium; refrigerant.

## 1. INTRODUCTION

The binary system of difluoromethane and pentafluoroethane (R32-R125) is regarded as a promising alternative actuating fluid to replace some of the ozone depleting conventional refrigerants. The purpose of the present study is to provide additional  $P$ - $V$ - $T$ -data needed to accomplish the equation of state of the above binary mixture that would be valuable for its further application to a refrigeration industry. The isochoric measurements were extended into two-phase region, so that vapor-liquid equilibrium parameters would be used to determine the parameters of critical point and the coefficients of the Benedict-Webb-Ruben equation of state.

## 2. EXPERIMENT

The measurements were performed along the isochores in the piezometer, which has been described in detail in our previous publication [1], thus only a brief description of the device is given here.

The piezometer represents a cylindrical vessel made of stainless steel with wall thickness of 1 mm. It is surrounded with two isothermal radiation shields and placed into a vacuum chamber. On the top part of the piezometer, there are a valve for filling the piezometer with refrigerant sample and a membrane separator. The latter detaches the inner space filled with investigated fluid from a communication capillary filled with nitrogen, which is used to compensate the pressure on the membrane and to transfer the pressure impulse to a tensometric pressure transducer and to a piston-type pressure gauge. Inside the piezometer, along its axis, the case with a platinum resistance thermometer is mounted. The precise electric heaters, which are governed by the signal of temperature difference between

the isothermal radiation shields and piezometer, are wound on outside of the piezometer, shields and membrane separator.

The automatic system allows maintaining the specified temperature inside the piezometer with uncertainty of  $\pm 5 \cdot 10^{-4}$  K, the vacuum chamber pressure being  $1.3 \cdot 10^{-4}$  Pa. The platinum resistance thermometer measures the temperature of sample with  $\pm 0.02$  K uncertainty. The density of the investigated fluid is defined by the following formula:  $\rho = m/V(T, P)$ , where  $m$  – mass of a fluid sample;  $V(T, P)$  – volume of the piezometer;  $T$  and  $P$  – temperature and pressure inside the piezometer, respectively.

The sample of binary refrigerant mixture is prepared in a special vessel by weighing. The mixture composition is determined with a standard error of about 0.01 mass fraction. The sample is loaded from a vessel into the initially vacuumized piezometer through a piezometer valve and capillary. To provide mixture composition constancy, all loading and unloading operations are performed in the conditions when the same phase (vapor or liquid) is established in the whole system (vessel-capillary-piezometer). Before and after loading (unloading), the vessel is weighed. The sample mass is defined by difference with uncertainty of  $\pm 0.0005$  g.

The volume of piezometer at the given temperature and pressure is defined as:

$$V(T, P) = V_{20} (1 + k P) [1 + 3\alpha (T - 293.15)] \quad (1)$$

In Eq. (1),  $\alpha$  is the thermal extension coefficient of the stainless steel, and  $k$  is the experimentally determined isothermal expansion coefficient,  $k = 3.2613 \cdot 10^{-6}$  MPa. The volume of piezometer at 293.15 K ( $V_{20} = 73.225 \text{ cm}^3$ ) was determined with an uncertainty of 0.06% by calibration using the distilled water.

It is evaluated that the values of density of the investigated samples are measured with a standard error of no more than 0.1% with 0.95 probability.

### 3. RESULTS

For the R32-R125 refrigerant mixture containing 0.1902 weight fraction of R32 we have obtained the experimental  $P$ - $V$ - $T$  data on 15 isochores in the liquid, gas and coexisting phases at temperatures ranging between 270 and 385 K and pressures of 0.7 to 8.0 MPa. The measured density covered the range of  $0.033 \cdot 10^3$  to  $1.06 \cdot 10^3$  kg/m<sup>3</sup>. The experimental results are presented in Table I and are shown in Figs. 1 and 2.

The boiling and condensation curves of a mixture are determined as the locus where the value of  $(\partial P / \partial T)_V$  has a discontinuous variation as it transmits from the one-phase region to the two-phase one. The parameters of the bubble and dew points are presented in Table II. The temperature dependence of the phase equilibrium curves is approximated by the following equations:

$$\ln P'' = -19966.27171 T^{-2} - 2204.87448 T^{-1} + 8.0341 \quad (2)$$

$$\ln P' = -31162.86337 T^{-2} - 2144.91598 T^{-1} + 7.97394 \quad (3)$$

In Eq. (2,3),  $P''$  and  $P'$  are the pressure values (in MPa) at the boiling and condensation curves, respectively. The temperature dependencies of the coexistence curve for pressure and density is shown in Fig. 3 and 4.

The cubic equation of state was applied in the works published in [3,4] for the R32-R125 refrigerant mixtures. The coefficients of this equation were found out on a basis of own experimental data and literary information. In the gas phase, the deviation of the

pressure values calculated by the equation of state [3,4] from our experimental results does not exceed 3.0% (see Fig. 5).

On the basis of our measurements, we determined the critical parameters of the investigated R32-R125 mixture (0.19021 mass fraction of R32) as follows:

$$\rho_C = 530 \text{ kg/m}^3; \quad T_C = 344.3 \text{ K}; \quad P_C = 4.3 \text{ MPa}.$$

In Fig. 3, the temperature dependence of density for the R32-R125 mixture (0.4377 mass fraction of R32), which we investigated in our previous study [5,6], is also presented. Both measurement series are in a good agreement. The values of the critical parameters are close to those calculated by method [4].

Experimental  $P$ - $V$ - $T$  data were described by the uniform equation of state in a form of Benedict-Vebb-Ruben correlation:

$$\frac{\pi \cdot \omega}{\tau} = Z = 1 + \frac{B}{\omega} + \frac{C}{\omega^2} + \frac{D}{\omega^5} + \frac{c_4}{\tau^3 \cdot \omega^2} \cdot \left[ \beta + \frac{\gamma}{\omega^2} \right] \cdot \exp \left[ -\frac{\gamma}{\omega^2} \right], \quad (4)$$

where:

$$B = b_1 - b_2/\tau - b_3/\tau^2 - b_4/\tau^3; \quad C = c_1 - c_2/\tau + c_3/\tau^2; \quad D = d_1 + d_2/\tau;$$

$$\pi = P/P_C; \quad \tau = T/T_C; \quad \omega = P_C/(\rho \cdot R \cdot T_C).$$

The parameters  $b_i$ ,  $c_i$  and  $d_i$  were determined by the linear least-squares method with fixed values of  $c_4$ ,  $\beta$  and  $\gamma$ . Further, with fixed  $b_i$ ,  $c_i$  and  $d_i$ , the deviation square function concerning parameters  $c_4$ ,  $\beta$  and  $\gamma$  was minimized. As a rule, such an iterative process is converged after the third or fourth pitch step. The standard deviation of the compressibility factor for all experimental points is  $\sigma = 0.92\%$ . The coefficients of the equation (4) are presented in Table III.

#### 4. CONCLUSION

The  $P$ - $V$ - $T$  data in the liquid, gas and two-phase states of the R32-R125 refrigerant mixture with mass fraction of R32 = 0.19021 are reported in this article. The experiments were performed in the temperature range from 270 to 385 K, at pressures of 0.7 to 8.0 MPa and in the density range from  $1.061 \cdot 10^3$  to  $0.03 \cdot 10^3$  kg/m<sup>3</sup>. The method of constant volume piezometer was used. The accuracy of the density measurements was not less than 0.1% (0.95). The experimental data on the gas and liquid isochores were approximated by polynomials. On this basis, the vapor-liquid coexisting curve was determined in a vicinity of critical region. The investigated refrigerant mixture R32-R125 with specified concentration is near-azeotropic mixture with temperature glide of less than 2 K. The uniform equation of state in a form of the Benedict-Webb-Rubens is applicable to describe the  $P$ - $V$ - $T$  data obtained with a standard deviation of the compressibility factor about 1%.

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Table I. Experimental Values of Density ( $\rho$ ) of the Investigated Refrigerant Mixture

$T$	$P$	$\rho$	$T$	$P$	$\rho$	$T$	$P$	$\rho$
(K)	(MPa)	(kg/m <sup>3</sup> )	(K)	(MPa)	(kg/m <sup>3</sup> )	(K)	(MPa)	(kg/m <sup>3</sup> )
Gas Phase								
272.57	0.6768	33.883	353.08	1.8408	73.122	371.29	3.7763	164.86
294.06	0.7667	33.846	360.39	1.8957	73.093	383.13	4.0214	164.75
311.23	0.8314	33.816	373.84	1.9967	73.04	337.15	3.6156	242.12
325.08	0.8795	33.791	382.82	2.0624	73.005	340.68	3.7492	242.07
338.39	0.9244	33.768	320.79	2.4353	136.13	350.88	4.1141	241.91
351.2	0.9677	33.746	327.14	2.5517	136.08	357.21	4.343	241.81
367.22	1.0207	33.717	335.46	2.7021	136.02	367.42	4.6946	241.66
379.73	1.0607	33.695	342.2	2.8158	135.97	375.83	4.9771	241.53
289.47	0.9917	47.077	348.35	2.9197	135.92	383.01	5.2154	241.42
303.32	1.0677	47.043	356.07	3.0482	135.86	339.64	3.9952	337.94
309.53	1.0997	47.028	359.96	3.1129	135.83	343.83	4.22	337.85
315.46	1.1291	47.013	366.93	3.2267	135.78	347.63	4.4269	337.76
328.63	1.1956	46.981	376.56	3.3888	135.7	353.17	4.7229	337.63
339.99	1.2507	46.953	382.88	3.4888	135.65	354.17	4.7739	337.61
350.93	1.3027	46.926	323.479	2.6962	165.32	354.18	4.7739	337.61
360.89	1.3505	46.901	327.039	2.8103	165.29	354.18	4.7739	337.61

Table I. (*Continued*)

$T$	$P$	$\rho$	$T$	$P$	$\rho$	$T$	$P$	$\rho$
(K)	(MPa)	(kg/m <sup>3</sup> )	(K)	(MPa)	(kg/m <sup>3</sup> )	(K)	(MPa)	(kg/m <sup>3</sup> )
368.78	1.39	46.881	333.434	2.9414	165.23	354.22	4.7768	337.6
379.01	1.437	46.856	335.17	3.0182	165.29	358.07	4.9766	337.52
301.86	1.4322	73.322	342.71	3.1849	165.14	362.12	5.1887	337.42
312.05	1.5134	73.282	349.91	3.3428	165.07	369.16	5.5466	337.26
330.03	1.6623	73.212	349.91	3.335	165.07	375.61	5.8712	337.11
339.33	1.7339	73.175	357.4	3.4821	165.0	383.75	6.2723	336.93
Liquid Phase								
336.614	3.67519	509.519	347.86	6.9365	873.63	337.87	7.763	983.52
344.498	4.4107	509.19	349.57	7.3092	873.45	337.87	7.761	983.53
349.173	4.85201	508.993	350.68	7.5642	873.32	337.87	7.7591	983.53
353.327	5.19524	508.827	351.96	7.8525	873.18	337.87	7.7616	983.53
358.098	5.63655	508.629	332.91	3.716	875.23	318.76	2.7478	1009.5
364.373	6.17592	508.374	332.93	3.7111	875.23	319.35	2.92	1009.4
370.62	6.75845	508.113	333.12	3.7434	875.21	320.14	3.1583	1009.3
376.419	7.26846	507.875	329.07	3.7382	936.72	322.7	3.9605	1008.9
381.562	7.71952	507.665	330.11	4.0128	936.59	325.77	4.9791	1008.4
342.92	4.3694	664.79	330.69	4.1579	936.52	328.77	5.9392	1007.9

Table I. (*Continued*)

$T$	$P$	$\rho$	$T$	$P$	$\rho$	$T$	$P$	$\rho$
(K)	(MPa)	(kg/m <sup>3</sup> )	(K)	(MPa)	(kg/m <sup>3</sup> )	(K)	(MPa)	(kg/m <sup>3</sup> )
347.57	4.9382	664.51	331.37	4.3354	936.43	331.2	6.7159	1007.5
348.86	5.0951	664.43	333.04	4.7581	936.22	333.64	7.4965	1007.1
352.97	5.6089	664.17	335.66	5.4446	935.88	318.51	2.7731	1012
357.2	6.1493	663.91	339.1	6.3546	935.43	319.53	3.0899	1011.8
361.91	6.7505	663.62	341.15	6.8705	935.18	321.28	3.6518	1011.6
366.09	7.2938	663.36	344.45	7.7433	934.75	311.78	2.1623	1012.5
369.32	7.7115	663.15	323.402	2.9374	969.85	314.9	2.3183	1012.3
372	8.0901	662.98	323.52	3.1658	969.77	317.71	2.5232	1012.1
338.676	4.057	803.36	324.86	3.5306	969.59	318.5	2.7596	1012
340.95	4.5683	803.13	326.09	3.8552	969.43	322.9	4.1541	1011.3
343.93	5.0782	802.87	329.34	4.6878	969	324.36	4.6484	1011.1
345.37	5.3381	802.74	331.65	5.3311	968.68	325.34	4.933	1010.9
348.04	5.8167	802.5	334.93	6.2667	968.21	327.21	5.5179	1010.6
350.12	6.1991	802.32	337.5	7.0002	967.85	328.91	6.0915	1010.3
352.36	6.611	802.12	339.2	7.4827	967.61	331.69	6.9868	1009.9
354.31	6.9739	801.94	340.77	7.9338	967.39	311.66	2.3149	1057.8
356.37	7.3564	801.75	321.24	2.7704	985.99	313.77	3.1058	1057.4

Table I. (*Continued*)

$T$	$P$	$\rho$	$T$	$P$	$\rho$	$T$	$P$	$\rho$
(K)	(MPa)	(kg/m <sup>3</sup> )	(K)	(MPa)	(kg/m <sup>3</sup> )	(K)	(MPa)	(kg/m <sup>3</sup> )
333.43	3.817	870.4	321.99	2.9891	985.88	316.14	3.9168	1057
335.63	4.2495	870.18	322.46	3.1284	985.81	318.93	4.9328	1056.5
339.6	5.1076	869.76	320.91	2.6724	986.04	321.46	5.8625	1056.1
341.74	5.5783	869.53	332.36	6.0694	984.35	324.193	6.5121	1055.7
344.7	6.2304	873.98	334.58	6.7627	984.02	326.648	7.4842	1055.2

Table II. Parameters of the Dew and Bubble Points of the Investigated Refrigerant Mixture

$T$	$P$	$\rho$	$T$	$P$	$\rho$
(K)	(MPa)	(kg/m <sup>3</sup> )	(K)	(MPa)	(kg/m <sup>3</sup> )
Dew point parameters			Bubble point parameters		
270.15	0.6761	33.889	339.95	3.8757	664.8
283.0	0.9581	47.1	360.0	3.674	803.44
294.84	1.3725	73.335	331.59	3.3974	875.44
316.4	2.3707	136.18	327.1	3.0913	936.97
323.48	2.7824	165.32	322.28	2.824	969.8
333.77	3.5136	242.18	321.4	2.6623	986
339.26	3.896	289.1	318.1	2.5131	1009.5
343.06	4.2245	349.6	317.65	2.4936	1012.2
			311.14	2.1316	1057.9

Table III. Coefficient of the Eq. (4)

i	$b_i$	$Ci$	$Di$
1	$1.69357 \cdot 10^{-1}$	$6.69044 \cdot 10^{-2}$	$2.13222 \cdot 10^{-4}$
2	$-9.155106 \cdot 10^{-3}$	$1.24110 \cdot 10^{-1}$	$-1.66508 \cdot 10^{-4}$
2	$5.90559 \cdot 10^{-1}$	$7.04118 \cdot 10^{-2}$	$\beta = 8.59706 \cdot 10^{-1}$
4	$-6.12298 \cdot 10^{-2}$	$3.67568 \cdot 10^{-2}$	$\gamma = 5.733585 \cdot 10^{-2}$

## FIGURE CAPTION

Fig. 1. Temperature dependence of pressure along gas isochores:

$P''$  – two-phase region; 1 –  $\rho \approx 33.0$ ; 2 –  $\rho \approx 47.0$ ; 3 –  $\rho \approx 73.3$ ; 4 –  $\rho \approx 146.2$ ; 5 –  $\rho \approx 165.3$ ; 6 –  $\rho \approx 242.2$ ; 7 –  $\rho \approx 509.7 \text{ kg/m}^3$ .

Fig. 2. Temperature dependence of pressure along liquid isochores:

$P'$  – two-phase region; 1 –  $\rho \approx 509$ ; 2 –  $\rho \approx 664$ ; 3 –  $\rho \approx 803$ ; 4 –  $\rho \approx 875$ ; 5 –  $\rho \approx 937$ ; 6 –  $\rho \approx 969.7$ ; 7 –  $\rho \approx 986$ ; 8 –  $\rho \approx 1009.5$ ; 9 –  $\rho \approx 1012.2$ ; 10 –  $\rho \approx 1057.9 \text{ kg/m}^3$ .

Fig. 3. Temperature dependence of pressure on the boiling and condensation curves:

1 and 3 – experimental dew and bubble points, respectively; 2 and 4 – temperature dependencies of the boiling and condensation curves, respectively.

Fig. 4. Temperature dependence of density of the coexisting phases for two series of data:

1 – mass fraction of R32 = 0.19021; 4 – mass fraction of R32 = 0.4377 [5]; 2 and 3 – critical density of R32 and R125, respectively.

Fig. 5. Deviation of pressure values calculated by equation of state [3,4] from the present experimental data:

1 –  $\rho \approx 33.8$ ; 2 –  $\rho \approx 47.1$ ; 3 –  $\rho \approx 73.3$ ; 4 –  $\rho \approx 136.1$ ; 5 –  $\rho \approx 165.3$ ; 6 –  $\rho \approx 242.1$ ; 7 –  $\rho \approx 337.8 \text{ kg/m}^3$ .











